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Title of the Invention: Glass products which are not liable to contamination
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Inventor: Makoto Kume
c/o Nippon Ita Garasu K.K., 8 Doshumachi-4-chome, Higashi-ku, Osaka-shi, Osaka-fu, Japan
Inventor: Takashi Nozu
c/o Nippon Ita Garasu K.K., 8 Doshumachi-4-chome, Higashi-ku, Osaka-shi, Osaka-fu, Japan
Applicant: Nippon Ita Garasu K.K.
8 Doshumachi-4-chome, Higashi-ku, Osaka-shi, Osaka-fu, Japan
Agent: Patent Attorney K. Ono

# SPECIFICATION

## 1. Title of the Invention

Glass products which are not liable to contamination

## 2. Scope of the Patent Claims

1) Glass product which is not liable to contamination, characterized in that a thin film of titanium dioxide to which a trace amount of Pt, Rh and/or Pd has been added is formed on the surface.

## 3. Detailed Description of the Invention

### Industrial Field of Application

The invention concerns glass products, and especially glass products which not liable to contamination, which can be used as windows in buildings and vehicles and in other applications.

### Prior Art

Contamination with various organic materials including oily components such as fatty acids and the tar-like materials produced by automobile exhausts becomes attached to the surface of window glass which is generally exposed to the atmosphere and, as a result of this, visibility is reduced because of the strongly water repellant nature of the surface of the window glass and the formation of water droplet. (Tsuchihachi, "The Surface Chemistry of Glass" (Japanese), published by Nankodo, 1958; Oba, "Glass Surface Design" (Japanese), published by the Kindai Henshu Co., 1983, page 201)

Furthermore, a glass surface to which organic material contamination has become attached is water repellant and so water droplets are formed when water which contains silicates due to rain etc. makes contact and these can run down only with difficulty and the insoluble silicate compounds etc. are likely to be precipitated out on the glass after the water has evaporated with the formation of solid contamination.

Moreover, such organic contamination is likely to be deposited heterogeneously on the glass surface and so

there is a problem in that the moisture in the atmosphere is liable to condense on the glass surface and so-called misting is liable to occur (Tsuchihachi, "The Surface Chemistry of Glass" (Japanese), published by Nankodo, 1958, page 50). Consequently the glass must be cleaned regularly using a detergent or an organic solvent.

Problems to be Resolved by the Invention

The invention is intended to provide glass products with which the organic contamination which becomes attached to the glass surface in the way described above is quickly and automatically broken down and eliminated, and which have the capacity generally for the surface to remain clean.

Means of Resolving These Problems

In order to achieve the aforementioned objective, the present invention is characterized in that a thin film of titanium dioxide to which Pt, Rh and/or Pd has been added in a trace amount is formed on the surface of the glass product.

Any of the known methods, such as the CVD method, the spray method, the sol-gel method, the immersion method, the vacuum vapour deposition method or the sputtering method for example, can be used to form the abovementioned thin film.

Furthermore, trace amounts of Pt, Rh or Pd may be coated on the surface of a glass product on the surface of which a thin film of titanium dioxide of thickness about 0.05 $\mu$m has been formed beforehand, for example on the surface of infrared reflecting glass such as "Refuraito S" (trade name, Nippon Ita Garasu CO.). The known coating techniques indicated above can be used for coating in this case, but coating can also be achieved using the photodeposition method. The method itself is known (for example, see Oyo Butsuri, Vol.53, pages 916 to 933 (1984))

Action

If light of wavelength below about 450 nm is

directed onto a glass product of this invention then the organic material contamination which is attached to the glass surface is oxidatively degraded by the so-called photocatalytic action of the thin film of titanium dioxide. That is to say, electrons and positive holes are generated within the thin layer of titanium dioxide, which is a semiconductor, as a result of irradiation with light and these migrate to the surface of the thin film and react with the organic material and moisture which is attached to the surface, and the organic material is oxidized and ultimately becomes $CO_2$. If ultra-fine grains of Pt, Rh or Pd are loaded onto the thin titanium dioxide film at this time then the efficiency of the above-mentioned photocatalytic action is markedly improved. This fact has been reported before in connection with fine particles of titanium dioxide, and the inventors have discovered the same effect can also be realized with a thin film of titanium dioxide.

Illustrative Examples

The coating conditions, with the spray method or the photodeposition method, are shown in Table 1. The amount of Pt, Rh and/or Pd attached was from 2 to 40 $mg/m^2$. The compositions of the coating liquids are shown in Table 2. The change in the angle of contact with water with respect to the duration of irradiation with light from a 500 W high pressure mercury lamp of each glass sample which had been exposed to the atmosphere is shown in Figure 1. Measurement of the angle of contact was carried out using a contact angle meter CA-D (manufactured by Kyowa Kaimen Kagaku). The lamp - sample distance was set at 20 cm.

Comparative Example 1 was normal front windshield glass and Comparative Example 2 was Refuraito S (titanium dioxide coated glass).

With the glass samples which had been made in accordance with the invention the angle of contact was seen to fall rapidly when compared with the comparative

examples. That is to say, the surface which was initially water repellant became easily wet with water because the organic material contamination was degraded and eliminated by the photocatalytic action.

As seen above, with glass sheets which conformed with the invention the contact angle with water under normal use conditions was very low, which is to say that the glass is easily wetted, and so it is clear that it is very difficult for the glass to become contaminated.

**Table 1**

| No. | Glass | Coating Method | Coating Liquid |
|---|---|---|---|
| 1 | Front Glass | - | - |
| 2 | Refuraito S | - | - |
| 3 | Refuraito S | Spray method | A |
| 4 | Refuraito S | Photodeposition | B |
| 5 | Refuraito S | Photodeposition | C |
| 6 | Front Glass | Spray method | D |
| 7 | Refuraito S | Photodeposition | E |

**Table 2**

| | | |
|---|---|---|
| A: | N,N-Dimethylformamide | 100 parts |
| | Chlorobenzonitrile platinum | 0.10 part |
| B: | Water | 80 parts |
| | Ethyl alcohol | 20 parts |
| | Rhodium chloride | 0.15 part |
| C: | Water | 80 parts |
| | Ethyl alcohol | 20 parts |
| | Palladium chloride | 0.20 part |
| D: | N,N-Dimethylformamide | 100 parts |
| | Titanium acetylacetone | 1.0 part |
| | Chlorobenzonitrile platinum | 0.10 part |
| E: | Water | 80 parts |
| | Ethyl Alcohol | 20 parts |
| | Potassium chloroplatinate | 0.05 part |

## Effect of the Invention

As described above, glass of this invention has a nature such that it very unlikely to become contaminated since, as a result of being coated with a thin film of titanium dioxide to which a trace amount of platinum, rhodium and/or palladium has been added, any organic

material attached to the glass surface is rapidly degraded by the action or ultraviolet radiation. Furthermore, the abovementioned thin films can be coated on a large surface area of glass sheet with a mass production system using a CVD method, a sputtering method or a spray method, for example, as the method of manufacture.

## Brief Explanation of the Drawing

Figure 1 is a graph which shows the change in the angle of contact with water with respect to the period of irradiation with a high pressure mercury lamp (400 W). No.1: Comparative example (front windshield glass), No.2: Comparative example (Refuraito S), Nos.3 to 7: Illustrative examples of the invention.

Applicant: Nippon Ita Garasu K.K.

Agent: Patent Attorney K. Ono

Figure 1